

Formation of coral concretions on marine iron

Neil A. North

Department of Material Conservation and Restoration, Western Australian Museum, Fremantle Branch, Finnerty Street, Fremantle, W.A. 6160

Introduction

In many shipwrecks excavated by marine archaeologists, numerous cast and wrought iron objects are found. Except for those wrecks which occur in atypical environments, such as the *Wasa* (Arrhenius *et al.*, 1973), these iron objects are generally encrusted with a layer of hard concretion. This concretion forms a semi-permeable barrier between the iron and the seawater on the wreck site and tends to modify the corrosion behaviour of the iron. The mechanism of corrosion in turn determines the conservation process required for stabilizing the iron against further deterioration. For the conservation procedures and for detailed examination, the iron artefact has to be separated from the concretion. As the concretion is often considerably harder than the partially, or wholly, corroded iron, this separation can present a problem to both the marine archaeologist and the conservator.

Due to the importance of iron concretions in both the corrosion and conservation of marine iron, an investigation into its properties, composition and mode of formation was undertaken. In this paper we will consider only the concretions found on marine iron lying on or above the sea-bed in regions of active sedentary epifauna growth. The concretions formed under anoxic conditions, i.e., buried under sediment or exposed to anoxic waters, will be dealt with in a later publication. The concretions described in this paper all came from the wreck of the *Batavia* which is currently being excavated by the West Australian Museum. A detailed description of the excavation and the wreck site has been given by Green (1975).

Batavia wreck site and water state

The wreck of the Dutch East Indiaman *Batavia* (1629) is located in the Wallabi Group of the

Houtman Abrolhos at approximately 28° 30' south and 113° 45' east. The wreck site forms a depression approximately 5 m X 15 m on the seaward side of Morning Reef. The reef areas surrounding the depression are 1 to 3 m below sea-level, whilst the depression itself is 2 to 6 m below sea-level. The incoming waves from the Indian Ocean normally break approximately 20 m beyond the innermost section of the wreck site in calm weather but with rougher seas they can break on, or before reaching, the site. These waves are accompanied by a strong alternating underwater surge which can readily carry a diver backwards and forwards over distances of 3 to 4 m.

The combined effect of the breaking waves and the underwater surge is to produce a very uniform, well oxygenated water body over the whole of the wreck site. The water temperature, in May, was found to be 24.5°C with a variation of $\pm 0.1^\circ\text{C}$ over different sections of the wreck site. The dissolved oxygen content of the water was determined, by Winklers' method, at various positions and depths on and near the wreck site and was found to be 4.3 ± 0.2 ml per litre and, within experimental error, no consistent variation was detected. The water salinity and pH were respectively, $34.8 \pm 0.2\text{‰}$ S (p.p.t.) and 8.15 ± 0.05 , again with no variation between sampling points. Temperature and salinity data have been collected monthly from November 1969 to March 1973 at Rat Island approximately 50 km south of the wreck site (West Australian Marine Research Labs, pers. comm.). These show an annual water temperature range of 5°C with mean annual temperature occurring in May–June. The salinities show an annual range of 0.05‰ S with minimum salinity occurring in June. Similar temperature and salinity fluctuations should also occur on the *Batavia* wreck site.

Sedentary epifauna growth

The *Batavia* wreck site is located in sub-tropical waters near the southern limit of active growth of calcareous reef forming coral and consequently massive coral growths are very infrequent in this area. The water conditions are favourable, however, for the prolific growth of coralline algae, which spreads in the form of a thin layer across the surface of suitable materials. Coralline algae, unlike the soft algae, has a partial exoskeleton of CaCO_3 on its outer surface. This exoskeleton remains after the death and decay of the organism and is subsequently overlaid by later growths of coralline algae. In time, quite substantial layers of CaCO_3 are formed over the surfaces of suitable materials and, in this respect, coralline algae is similar to the reef forming corals. Any biologically inert material which remains stationary on the wreck site is very rapidly covered by a layer of coralline algae; this occurs on wreck remains, modern debris and natural materials such as dead coral lumps. If undisturbed the layers of calcium carbonate from the coralline algae build up progressively, and merge with similar growths on adjacent bodies to form a continuous surface over quite large areas. This layer, once formed, seems to provide a suitable substrate for a secondary growth of seaweed, soft corals, molluscs and occasionally, hard calcareous corals.

The formation rate of sedentary epifauna can be gauged from some observations made with objects placed on the wreck site during the excavation work. After three months' immersion, a number of house bricks were found to have approximately 25% surface coverage of coralline algae. After 12 months on the sea-bed, some iron marker stakes were completely covered with coralline algae and secondary growths, all seaweeds, were also present. An iron mooring anchor, after three years' immersion, was covered by 0.01 m thick layer of coralline algae which, in turn, supported a varied and prolific secondary growth.

Iron concretions

The concretions which form on iron objects on the wreck site are externally indistinguishable from those formed on natural materials, such as large coral fragments. However, if a section is broken from an iron concretion the underlying layers are, initially, black to yellow in colour. Over a period of 3 to 24 hours, on the sea-bed, the freshly exposed surface changes to a rust-red colour which also stains the adjacent undamaged surfaces of the concretion. This colour change is accelerated if the concretion is exposed to the atmosphere.

When an iron concretion is dried, two distinct zones are apparent on the section along the direction of growth (Fig. 1). The outer or

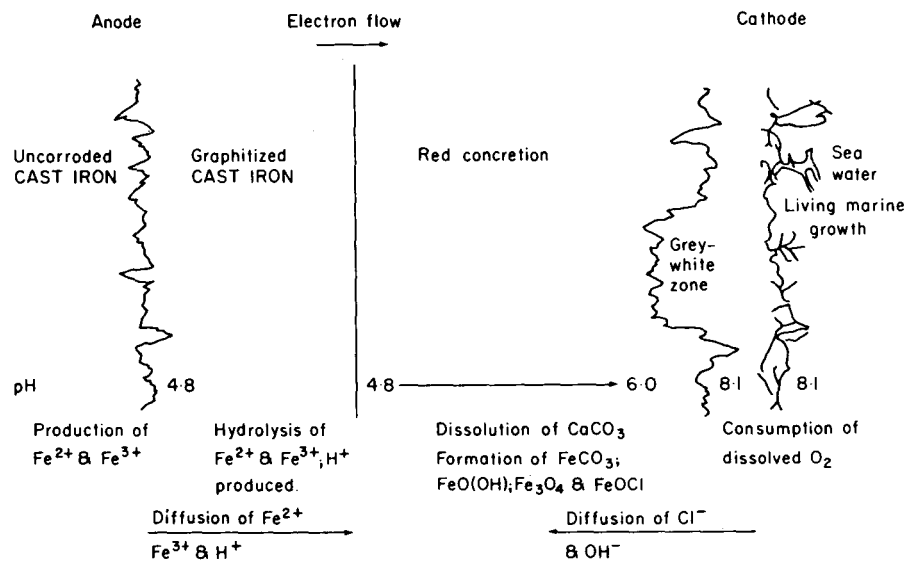


Figure 1. Diagrammatic cross-section of concretion on *Batavia* cast iron.

surface zone is greyish white and appears identical to the surface layers of concretion on natural materials. The inner zone, which comprises more than 90% of the concretion is red-brown in colour and extends inwards to the original surface of the iron object. The chemical composition of both zones was determined and is shown on Table 1. For comparison purposes the chemical composition of a sample of reef coral from this site is also shown in Table 1.

from the white outer zone. In particular, the Fe content is very high (50% by weight) whilst the Ca and Mg are so reduced in concentration as to be almost absent. However, the presence of appreciable amounts of organic carbon, carbonate and silica suggest that this red zone was originally formed in a similar manner to the outer white zone. To clarify this point thin sections of the red concretion were examined using both an optical microscope, with polariser, and by X-ray diffraction.

Table 1

Composition of concretions and reef material

Element	Reef material (wt %)	Outer white zone	Iron concretion (wt %)	
			Inner red zone (4 cm below seaward surface)	Inner red zone (25 cm below seaward surface)
Fe (total)	Absent	1.2	53.2	49.8
Fe ³⁺	Absent	1.2	47	45
Ca ²⁺	32.9	34.6	0.22	0.08
Mg ²⁺	3.5	2.5	0.07	0.01
Na ⁺	0.56	0.74	0.12	0.16
S ₁ O ₂	0.35	0.25	0.64	0.15
S (total)	ND	ND	2.2	2.5
CO ₃ ²⁻	54.8	55.5	8.7	3.4
Organic Carbon (excluding CO ₃ ²⁻)	ND	ND	2.6	1.9
P	ND	ND	0.18	0.39
Cl	0.15	1.7	6.35	9.90

ND, not determined.

The outer zone of iron concretion

From Table 1 it is seen that the white outer zone of the iron concretion has basically the same composition as the reef material. The major difference is the presence of up to 2% iron in the iron concretion surface and this is presumably due to diffusion from the underlying iron rich, red layer. Apart from this trace of iron, no significant differences were detected, either chemically or biologically, between these samples. From this it would appear that the outer surface layers of the iron concretion are growing, or accumulating, in the same manner as the surface layers on all other immobile objects on or near the wreck site.

The inner zone or iron concretion

The inner red-brown zone, as seen in Table 1, differs considerably in chemical composition

Microscope and X-ray diffraction examination

The microscope examination showed that the red concretion was generally composed of particles in the size range 0.0001 to 0.0003 m with the occasional larger piece. These particles were mostly of organic origin and consisted of fragmentary corals, molluscs, foraminifera and others with organic type textures. The particles were partially eroded, poorly sorted and of random orientation. The mixture was cemented together by an opaque material, black to red in colour. This material was subsequently identified by X-ray diffraction to be principally FeO(OH) (limonite) with some Fe₃O₄ (magnetite).

The original CaCO₃ (calcite) skeletal material was found to be converted into various iron compounds with FeCO₃ (siderite) being the most common. Generally this replacement pro-

cess had gone to completion but occasionally a skeletal structure was observed which retained a core of unaltered CaCO_3 . Even in cases of complete replacement of the CaCO_3 , the organic texture of the skeletal material was still obvious. In a number of cases, FeO(OH) was observed to have been deposited inside cavities in the skeletal structure whilst the structure itself was converted to FeCO_3 . For example, the normally open spaces within a coral fragment were filled with FeO(OH) whilst the coral itself was converted to FeCO_3 . Broadly speaking, the extent of CaCO_3 replacement was found to increase with increasing distance inwards from the concretion water surface but some pieces, generally bulky mollusc fragments, were not completely transformed even when located near the original iron surface. Other types of organic CaCO_3 , in particular that of the coralline algae which forms the binding cement in the outer layer, seemed to be very readily attacked and were completely replaced by FeO(OH) and Fe_3O_4 .

To verify the identity of the compounds composing the red concretion, samples were analysed by X-ray diffraction and electron microprobe. These showed that the major components were FeO(OH) (limonite), Fe_3O_4 (magnetite), FeCO_3 (siderite) and FeOCl . Minor constituents were CaCO_3 (calcite), SiO_2 (quartz) FeS and elemental sulphur. Traces of NaCl and $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) were occasionally found.

In situ acidities

The substitution and precipitation products found in the inner red concretion suggest the outward diffusion of an iron rich slightly acidic solution from the corroding iron object towards the concretion-sea-water interface. To test this hypothesis the pH's inside a concretion and the graphitized regions of corroding cast iron were measured.

The pH measurements were carried out by selecting a relatively small concreted cast iron object, e.g. a cannon ball, which had an intact concretion. After raising the concreted object from the sea-bed to the workboat, it was immediately dried with a cloth to remove any surface sea-water which could have contaminated the interior and so given false pH values. The concretion was then broken open with a

hammer and the pH's across the freshly cleaved surface and into the graphitized zone were immediately measured using a flat surface pH electrode (METROHM) and a portable pH meter which had previously been calibrated. The freshly cleaved surfaces contained sufficient moisture to obtain pH readings without having to add additional water. The entire pH measuring process took approximately 10–15 minutes from the time the concreted object was removed from the sea and the possibility of pH change due to sample deterioration was therefore minimized.

The pH inside the graphitized regions of cast iron and in the red concretion near the original metal surface was found to be 4.8 ± 0.1 with very little variation between different samples. Further out towards the concretion-sea-water interface, the pH of the red concretion rose, slowly and irregularly, to a maximum value of between 5.5 and 6.5. At the interface of the red and white concretion layers the pH increased abruptly to 8.1 which is the same as the pH of the sea-water as determined by *in situ* pH measurements.

The higher acidity of the interstitial water in the red concretion or graphitized regions compared with that of sea-water could be due either to a crevice-type iron corrosion, where the anodic and cathodic reactions are well separated physically, or to the presence of sulphate reducing bacteria. In the innermost regions of the red concretion the former process is probably dominant. In this case the pH is close to the values of 2.7–4.7 which Pourbaix (1972) observed inside crevices in corroding iron, but it is much lower than the pH's of 6 to 7 usually produced by sulphate reducing bacteria, in anoxic marine sediments (Gardner, 1973).

In the outer regions of the red concretion, where the pH lies between 5.5 and 6.5 the conditions are favourable for sulphate reducing bacteria and the presence of appreciable sulphides and elemental sulphur in the concretion confirms their presence.

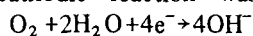
Iron concretion formation mechanism

From the observations described above it appears that on the *Batavia* wreck site the iron concretion was formed in the following manner:

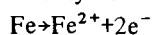
In the two to three years immediately after the shipwreck, the iron objects on the wreck

site were covered with a layer of coralline algae and this provided a suitable substrate for a secondary growth of seaweeds, hard corals, molluscs etc. The very rough outer surface, so produced, provided a good trap for sand particles, coral fragments and other debris which were swept off the bottom by wave action and deposited on the concretion surface. Subsequent growth of the coralline algae overlaid both the secondary growth and the sea bottom debris and incorporated them into the concretion. This growth produced a layer of low porosity on the surface of the iron which greatly retarded the interchange of dissolved species between the metallic iron and the water column. The dissolved oxygen in the entrapped water, in contact with the metallic iron, was rapidly depleted and the dominant cathodic reaction in the iron corrosion process then became the conversion of dissolved oxygen at the coralline algae-sea-water interface.

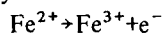
The situation then consisted of that shown in Fig. 1. At the coralline algae-sea-water interface the cathodic reaction was probably:



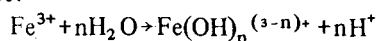
At the metallic iron surface the anodic reaction would probably be:



and subsequently



The ferrous and ferric ions so produced would be rapidly hydrolysed through reactions of the type:

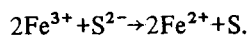
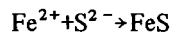


The combined effect of the anodic and hydrolysis reactions was to produce an acidic iron rich solution at the surface of the metallic iron.

Charge neutrality in this system was maintained by the diffusion outwards, away from the metallic iron, of cations and a corresponding inward diffusion of anions. The diffusing anions would be Cl^- ions as these are the anions with the highest transport number in sea-water. The outward diffusing cations were, in the initial stages of diffusion, Fe^{2+} , Fe^{3+} and H^+ .

During this outward diffusion through the concretion, some ferrous ions interchanged with the calcium in the CaCO_3 concretion to produce FeCO_3 . Some of the skeletal and cementing calcite would also dissolve, thus causing the pH of the diffusing solution to increase, and with increasing pH the ferrous and

ferric ions will precipitate out as oxides, hydrated oxides and oxychlorides. These form an iron cementing matrix to replace the original calcite matrix which is slowly dissolving. When the outward diffusing iron rich solution, now containing appreciable quantities of calcium, comes into contact with the inward diffusing alkaline solution, rich in chlorides, the pH rapidly increases to that of sea-water and virtually complete precipitation of the remaining iron occurs. Due to the high Cl^- content, the relatively low OH^- concentration, and the presence of appreciable dissolved oxygen in the adjacent sea-water, the main precipitation products at this point are $\text{FeO}(\text{OH})$ and FeOCl . The FeS and elemental sulphur found in the concretion is probably formed through the reaction of Fe^{2+} and Fe^{3+} ions with S^{2-} ions produced by sulphate reducing bacteria. The reactions in this case being:



The end result of all these reactions is that the inner concretion becomes a replica of the marine growth and deposition, with the CaCO_3 of the marine organisms virtually entirely replaced by iron corrosion products.

Conclusion

From observations and experiments on iron concretions from the *Batavia* wreck we have been able to postulate a mechanism for the formation of concretions on iron objects lying on or above the sea-bed in aerated waters. Although we have only studied concretion formation on a warm sub-tropical site, the same general mechanism should also apply to other sites but with corresponding changes in the organic material from which the concretion is formed. For example, in temperature waters, we would expect siliceous diatoms, foraminifera and bivalve molluscs to take the place of the coralline algae and corals found on the *Batavia* site. Preliminary studies on the concretions formed on iron objects buried beneath sea floor sediments, indicate that these concretions are formed in a different manner to that described in this paper. Further studies on buried marine iron are being carried out and it is intended to report on these at a later date.

Acknowledgements

The author wishes to thank the many people who have assisted with this work. In particular thanks are due to the Maritime Archaeology Department, WA Museum, and Jeremy Green for help, advice and patient forbearance in the field; to John Clarke for assistance with mineral

identification; to Shirley Slacksmith for assistance with biological aspects; to Colin Pearson for advice and discussions and to Mike Owens for assistance in both field and laboratory work. I wish also to thank the Australian Research Grants Committee for provision of funds for this work.

References

- Arrhenius, O., Barrman, L. and Sjostrand, E., 1973, *Conservation of old rusty iron objects*. Bulletin No. 61E, Swedish Corrosion Institute, Stockholm.
- Gardner, L. R., 1973, Chemical models for sulphate reduction in closed anaerobic marine environments. *Geochimica et Cosmochimica Acta*, 37: 53-68.
- Green, J. N., 1975, The VOC Ship *Batavia* wrecked in 1629 on the Houtman Abrolhos, Western Australia. *Int. J. Naut. Archaeol.* 4: 43-63.
- Pourbaix, M. 1972, Significance of protection pitting, intergranular corrosion and stress-corrosion cracking. *J. Less. Comm. Met.* 28: 51-69.